

**PATENT ABSTRACTS OF JAPAN**(11)Publication number : **05-140395**(43)Date of publication of application : **08.06.1993**

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**C08L 33:12 )**(21)Application number : **03-305941**(71)Applicant : **MITSUBISHI PLASTICS IND LTD**(22)Date of filing : **21.11.1991**(72)Inventor : **ISHII MIKITO**  
**ITO SHOJI****(54) VINYL CHLORIDE-BASED RESIN COMPOSITION**

(57)Abstract:

PURPOSE: To obtain the subject composition good in calender sheet production rate, transparency and fluctuation in thickness by adding respective copolymers of methyl methacrylate and butyl acrylate and butyl methacrylate each having a specific molecular weight to a vinyl chloride-based resin.

CONSTITUTION: The objective vinyl chloride-based resin composition is obtained by adding 0.5-1.5 pts.wt. copolymer, composed of 82-90wt.% methyl methacrylate and 8-10wt.% butyl acrylate and having 1600000-2000000 molecular weight, 0.5-1.5 pts.wt. copolymer, composed of 55-61wt.% methyl methacrylate and 45-39wt.% butyl methacrylate and having 100000-500000 molecular weight and 0.1-0.7 pt.wt. copolymer, composed of 54-60wt.% methyl methacrylate, 16-30wt.% butyl acrylate and 30-20wt.% butyl methacrylate and having 250000-650000 molecular weight to 100 pts.wt. vinyl chloride-based resin. The resin composition does not disturb balance among air inclusion, flow mark, transparency, fluctuation in thickness, etc., in spite of improvement in calender sheet production rate.

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CLAIMS

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[Claim(s)]

[Claim 1] It consists of 82 - 90% of methylmetaacrylates, and 18 - 10% of butyl acrylate to the vinyl chloride system resin 100 weight section. the copolymer of molecular weight 1,600,000-2 million The 0.5 - 1.5 weight section, It consists of 55 - 61% of methylmetaacrylates, and 45 - 39% of butyl methacrylate. molecular weight the copolymer of 100,000 to 500,000 The 0.5 - 1.5 weight section, The vinyl chloride system resin constituent which consists of 54 - 60% of methylmetaacrylates, 16 - 20% of butyl acrylate, and 30 - 20% of butyl methacrylate, and comes to carry out 0.1-0.7 weight section addition of the copolymer of molecular weight 250,000-650,000.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] About a vinyl chloride system resin constituent, even if especially this invention raises the production rate of calendered sheeting, it relates to the vinyl chloride system resin constituent which air winds, and is not crowded inside a sheet or does not break down the balance of (entering air), the flow mark, a thickness deflection, transparency, etc.

[0002]

[Description of the Prior Art] In order to raise a production rate and to prevent poor quality, such as entering air, conventionally, adding the resin (a following EVA system and abbreviated name) of an ethylene-vinyl acetate system as processing aid is performed.

[0003]

[Problem(s) to be Solved by the Invention] it was alike, and a certain grade, although an effect is accepted, since [ appropriate ] it improved a quality characteristic further, when addition of a EVA system resin made the addition of a EVA system resin increase, it had the problem that the balance of quality will collapse

[0004]

[Means for Solving the Problem] this invention -- this trouble -- it is going to solve -- the place which is a thing and is made into the summary It consists of 82 - 92% of methylmetaacrylates, and 18 - 10% of butyl acrylate to the vinyl chloride system resin 100 weight section. The copolymer of molecular weight 1,600,000-2 million is consisted of the 0.5 - 1.5 weight section, 55 - 61% of methylmetaacrylates, and 45 - 35% of butyl methacrylate. molecular weight the copolymer of 100,000 to 500,000 The 0.5 - 1.5 weight section, It consists of 54 - 60% of methylmetaacrylates, 16 - 20% of butyl acrylate, and 30 - 20% of butyl methacrylate, and is in the vinyl chloride system resin constituent which comes to carry out 0.1-0.7 weight section addition of the copolymer of molecular weight 250,000-650,000.

[0005] Hereafter, this invention is explained still in detail. Even if the vinyl chloride system resin which is a major component in this invention is usual vinyl chloride resin or the usual copolymer which has side chains, such as vinyl acetate, in part, it can be used effectively.

[0006] Tin system stabilizers, such as organic tin maleate series well-known as a stabilizer added by such vinyl chloride system resin and sulfur-containing organic tin maleate series, are used suitably, and addition number of copies is used in the range of 1 - 6 weight section to the vinyl chloride system resin 100 weight section. As other additives, number-of-copies addition of a plasticizer, a MBS system shock improvement agent, the lubricant, etc. is carried out suitably.

[0007] In this invention, especially the thing for which it consists of 82 - 90% of methylmetaacrylates and 18 - 60% of butyl acrylate, molecular weight consists of the copolymer, and 55 - 61% of methylmetaacrylates and 45 - 39% of butyl methacrylate of 1,600,000 to 200 to a vinyl chloride system resin, molecular weight consists of the copolymer, 54 - 60% of methylmetaacrylates and 16 - 20% of butyl acrylate, and 30 - 20% of butyl methacrylate of 100,000 to 500,000, and molecular weight uses the copolymer of 250,000 to 650,000 together

[0008] It consists of 82 - 90% of methylmetaacrylates, and 18 - 10% of butyl acrylate, as for molecular weight, the copolymer of 1,600,000 to 2 million has an effect mainly in prevention of entering air or the flow mark, and, as for addition number of copies, it is important to use in the range of the 0.5 - 1.5 weight section. Entering air arises that addition number of copies is [ molecular weight ] less than 1,600,000 under in the 0.5 weight section, it is not desirable, and since the flow mark will arise if an addition exceeds the 1.5 weight section and molecular weight exceeds 2 million, it is not desirable.

[0009] It consists of 55 - 61% of methylmetaacrylates, and 45 - 39% of butyl methacrylate, as for molecular weight, the copolymer of 100,000 to 500,000 has an effect mainly in prevention of entering air or the flow mark, and improvement in transparency, and, as for addition number of copies, it is important to use in the range of the 0.5 - 1.5 weight section. If an addition exceeds the 1.5 weight section, entering air occurs, and it will be bad opaque when molecular weight is as small as less than 100,000. Moreover, there are few additions as the less than 0.5 sections, and if molecular weight becomes large exceeding 500,000, it generates and is not desirable [ the flow mark ].

[0010] It consists of 54 - 60% of methylmetaacrylates, 16 - 20% of butyl acrylate, and 30 - 20% of butyl methacrylate, as for molecular weight, the copolymer of 250,000 to 600,000 has an effect mainly on a thickness deflection or a transparent disposition, and addition number of copies is used in the range of the 0.1 - 0.7 weight section. Transparency becomes bad and is not desirable, if a thickness deflection becomes [ addition number of copies ] bad under in the 0.1 weight section when molecular

weight is as small as less than 250,000, and an addition exceeds the 0.7 weight section, molecular weight exceeds 600,000 and it becomes large.

[0011] this invention is explained still in detail based on the example of an experiment below [the example of an experiment]. As opposed to the vinyl-chloride-resin 100 weight section of polymerization degree 700 The MBS system shock improvement agent 11 weight section, The dioctyl tin malate polymer 0.7 weight section, the dioctyl tin mercapto 1.3 weight section, JIISO nonyl horse mackerel peat 2.5 weight section addition is carried out. Copolymer [ which consists of copolymer / from methylmetaacrylate 87% and butyl acrylate 13% / (Following A and abbreviated name), and methylmetaacrylate 58%, and butyl methacrylate 42% ] (Following B and abbreviated name), and methylmetaacrylate 57%, and butyl acrylate 18% And the addition which consists of butyl methacrylate 25% (Following C and abbreviated name) was changed as shown in Table 1, and it rolled out to 0.5mm \*\* by the rolling temperature of 190 degrees C, and rolling speed 60 m/min, and entering air, the flow mark, transparency, and the thickness deflection were evaluated.

[0012] The result is shown in Table 1.

[0013]

[Table 1]

表 1

| No | A      |           | B      |     | C      |     | 評 価        |               |       |            |
|----|--------|-----------|--------|-----|--------|-----|------------|---------------|-------|------------|
|    | 添加量    | 分子量       | 添加量    | 分子量 | 添加量    | 分子量 | エ ア<br>入 り | フ ロー<br>マ ー ク | 透 明 性 | 厚 み<br>振 れ |
| 1  | 0.4PHR | 180万      | 1.0PHR | 30万 | 0.4PHR | 45万 | ×          | ○             | ○     | ○          |
| 2  | 1.6    | "         | "      | "   | "      | "   | ○          | ×             | ○     | ○          |
| 3  | 1.0    | "         | 0.4    | "   | "      | "   | ○          | ×             | ○     | ○          |
| 4  | "      | "         | 1.6    | "   | "      | "   | ×          | ○             | ○     | ○          |
| 5  | "      | "         | 1.0    | "   | 0.05   | "   | ○          | ○             | ○     | ×          |
| 6  | "      | "         | "      | "   | 0.8    | "   | ○          | ○             | ×     | ○          |
| 7  | "      | 85        | "      | "   | 0.4    | "   | ×          | ○             | ○     | ○          |
| 8  | "      | 280       | "      | "   | "      | "   | ○          | ×             | ○     | ○          |
| 9  | "      | 180       | "      | 5   | "      | "   | ○          | ○             | ×     | ○          |
| 10 | "      | "         | "      | 60  | "      | "   | ○          | ×             | ○     | ○          |
| 11 | "      | "         | "      | 30  | "      | 15  | ○          | ○             | ○     | ×          |
| 12 | "      | "         | "      | "   | "      | 95  | ○          | ○             | ×     | ○          |
| 13 | 0.5    | "         | 0.5    | "   | 0.1    | 45  | ○          | ○             | ○     | ○          |
| 14 | 1.5    | "         | 1.5    | "   | 0.3    | "   | ○          | ○             | ○     | ○          |
| 15 | 0.5PHR | 180万      | 1.5PHR | 30万 | 0.1PHR | 45万 | ○          | ○             | ○     | ○          |
| 16 | "      | "         | "      | "   | 0.7    | "   | ○          | ○             | ○     | ○          |
| 17 | 1.5    | "         | 0.5    | "   | 0.1    | "   | ○          | ○             | ○     | ○          |
| 18 | "      | "         | 1.5    | "   | "      | "   | ○          | ○             | ○     | ○          |
| 19 | 比      | EVA 3 PHR |        |     |        |     | ○          | ×             | ○     | ○          |
| 20 | 較      | "         |        |     |        |     | ○          | ○             | ○     | ○          |
| 21 | 例      | "         |        |     |        |     | ×          | ○             | ○     | ○          |

(注) A : メチルメタアクリレート 87%, ブチルアクリレート 13% の共重合体  
 B : メチルメタアクリレート 58%, ブチルメタアクリレート 42% の共重合体  
 C : メチルメタアクリレート 57%, ブチルアクリレート 18% 及び ブチルメタアクリレート 25% の共重合体を使用した。

[0014] Entering evaluation method (1) air and the flow mark carried out visual evaluation of the rolling sheet as follows.

○ -- It is few. x -- Many (2) transparency carried out visual evaluation of the rolling sheet as follows.

○ -- It is few. x -- Many (3) thickness deflections measured the thickness of a rolling sheet, and evaluated it as follows.

○ -- Smallness (inside of product specification) x -- Size (product substandard)

The ethylene vinylacetate copolymer (Following EVA and abbreviated name) was similarly estimated as the example of an experiment to the vinyl-chloride-resin 100 weight section about what carried out 3-7 weight section addition instead of the copolymer of A, B, and C of the same vinyl-chloride-resin constituent as the example of a [example of comparison] experiment.

[0015] The examples No13-No18 of an experiment equivalent to this invention article all showed the good result in the point of entering air, the flow mark, transparency, and a thickness deflection. As for that to which the molecular weight and the addition of a copolymer of A, B, and C added the thing and EVA of this invention out of range, any one of entering air, the flow mark, transparency, and thickness deflections showed the dissatisfied result.

[0016]

[Effect of the Invention] this invention can obtain a very good product in the point of entering air, the flow mark, transparency, and a thickness deflection irrespective of elevation of the production rate of calendered sheeting by [ which were described above ] carrying out the amount combination addition of specification of three sorts of specific copolymers like at a vinyl chloride system resin.

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[Translation done.]

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**C08L 51:00 )**(21)Application number : **05-026912**(71)Applicant : **mitsubishi rayon co ltd**(22)Date of filing : **16.02.1993**(72)Inventor : **matsumoto yoshiji**  
**kaneda masahiro****(54) PRODUCTION OF VINYL CHLORIDE RESIN COMPOSITION**

(57)Abstract:

PURPOSE: To produce a resin composition reduced in plate-out occurring during molding and suppressed in the formation of flow marks and fisheyes on the surface of a sheet by mixing a vinyl chloride resin with a specified two-stage polymer as a processing aid.

CONSTITUTION: A vinyl chloride resin namely polyvinyl chloride, a copolymer of at least 80wt.% vinyl chloride with a monomer copolymerizable therewith or a mixture thereof is mixed with 0.1-30 pts.wt. two-stage polymer having an  $\eta_{sp}/c$  ratio of 0.05 or above and a molecular weight distribution of 3.0 or below as determined by GPC as a processing aid. The polymer as the processing aid can be obtained by copolymerizing 99-70wt.% monomer (mixture) comprising 100-60wt.% methyl methacrylate and 0-40wt.% acrylic ester or methacrylic ester except methyl methacrylate with 30-1 wt.% monomer (mixture) comprising a monomer or monomers copolymerizable with (meth)acrylic ester.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The manufacture method of a vinyl chloride system resin constituent that consist of 1 % of the weight, and etasp/c consists of the monomer in which the monomer or the monomer (mixture i) 99-70 % of the weight, the methacrylic ester or the acrylic ester, and copolymerization which are characterized by providing the following are possible, or monomer mixture (ii) 30 0.05 or more and the two-step polymer (B) whose molecular weight distribution are 3.0 or less in GPC0.1 - the 30 weight sections. The vinyl chloride system (resin A) 100 weight section which consists of the copolymers or such mixture of a polyvinyl chloride or at least 80% of the weight or more of a vinyl chloride, and a this and the monomer which can be copolymerized. 100 - 60 % of the weight of methyl methacrylates, an acrylic ester, or 0 - 40 % of the weight of other methacrylic esters except a methyl methacrylate.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Industrial Application] The dissolution or plate out of the flow mark which it raises the processability when this invention is blended with a vinyl chloride system resin in more detail about the manufacture method of a vinyl chloride system resin constituent, and is generated on the sheet which carried out calender fabrication, a film or the sheet which carried out extrusion molding, and a film is related with the manufacture method of the vinyl chloride system resin constituent using the processing aid excellent in thermal stability with little [ it is few and ] heat coloring.

[0002]

[Description of the Prior Art] Since various kinds of physical properties and chemical property are excellent, the vinyl chloride system resin is widely used in various fields. However, since the temperature in which a fabricating operation is possible, and pyrolysis temperature are approaching, this resin has the trouble that the temperature field in which a fabricating operation is possible is remarkable, and it is inferior in processability that gelling speed is slow in \*\*\*\*\* again etc.

[0003] As a method of canceling this trouble, the method of blending a plasticizer with a vinyl chloride system resin is performed, and according to this method, in a certain grade, although improved, since the plasticizer blended at the time of hot forming vaporizes, the new problem that it being difficult to attain the purpose original enough and the mechanical property of mold goods obtained deteriorate produces the above-mentioned trouble.

[0004] Moreover, promote the gelling speed at the time of the fabricating operation of a vinyl chloride system resin, enable deep-drawing fabrication, or set at the time of a further prolonged fabricating operation. The gloss which does not change to a \*\*\*\*\* body surface is held, or the method of blending the copolymer which makes a methyl methacrylate a principal component for the purpose of the improvement in the so-called processability of making the front face of the obtained Plastic solid smooth etc. as processing aid is proposed (refer to JP,52-1745,B, JP,52-1746,B, and JP,53-2898,B).

[0005] Since it not only becomes possible, but the application of a vacuum forming, a profile extrusion, etc. of deep-drawing fabrication is attained as a result of the \*\*\*\*\* ductility in an elevated temperature increasing quickly [ the gelling speed at the time of a fabricating operation ] as for the vinyl chloride system resin constituent which blended the processing aid which consists of such a specific copolymer, the fabricating nature in a rigid-polyvinyl-chloride system pitch field is sharply improvable.

[0006] Moreover, generally the copolymer which is the processing aid blended into this vinyl chloride system resin is easily manufactured by the emulsion-polymerization method. However, although it can apply to a vacuum forming, a profile extrusion, etc. as a result of the increase of ductility [ the improvement of gelling speed and the \*\*\*\*\* ductility in an elevated temperature ] at the time of a fabricating operation when the processing aid created by the random polymerization is added to a vinyl chloride system resin, in the sheet in calender fabrication and extrusion molding, and a film, fish eyes occur frequently and it is not suitable for creation of a sheet and a film. Moreover, as shown in the example 1 of JP,52-1746,B, and the example 1 of JP,53-2898,B, when a graft polymer (two-step polymer) was added to a vinyl chloride system resin, in increase of an improvement of the gelling speed at the time of a fabricating operation, and the \*\*\*\*\* ductility in an elevated temperature, also in the sheet in a vacuum forming, a profile extrusion and calender fabrication, and extrusion molding, and a film, there was also no generating of a fish eye, and it might be good processing aid.

[0007] However, shortening (improvement in the speed) of the sheet in calender fabrication and extrusion molding and the cycle time of a film was achieved in recent years, in the above-mentioned processing aid, the flow mark and the plate out occurred during a sheet and film fabrication, and there was a trouble that the quality of mold goods will be spoiled.

[0008]

[Problem(s) to be Solved by the Invention] When this invention persons do a fabricating operation using the processing aid blended with a vinyl chloride system resin, The result wholeheartedly examined for the purpose of offer of the vinyl chloride system resin constituent which the above-mentioned trouble does not produce, At the time of the polymerization of a graft polymer (two-step polymer) used as an indispensable component, a methyl methacrylate By adding by the method near a package or it, in case the copolymer of the 1st step is not made into the dropping polymerization covering a long time like JP,53-2898,B, but a random copolymer is created and the polymerization of the 2nd step is carried out to the copolymer It found out that the processing aid by which molecular weight distribution became narrow, the amount polymer portion of macromolecules decreased in the film of high-speed calender fabrication and extrusion molding and the sheet, generating of the flow mark has been improved, and generating of a plate out has been improved further was obtained, and this invention was reached.



[0009]

[Means for Solving the Problem] The vinyl chloride system (resin A) 100 weight section which this invention becomes from the copolymers or such mixture of a polyvinyl chloride or at least 80% of the weight or more of a vinyl chloride, and a this and the monomer which can be copolymerized, The monomer which consists of 100 - 60 % of the weight of methyl methacrylates, an acrylic ester, or 0 - 40 % of the weight of other methacrylic esters except a methyl methacrylate, or monomer (mixture i) 99-70 % of the weight, It consists of a monomer or monomer mixture (ii) 30-1 % of the weight in which a methacrylic ester or an acrylic ester, and copolymerization are possible. and -- eta -- sp/c -- 0.05 -- more than -- moreover -- GPC -- molecular weight distribution -- 3.0 -- less than -- it is -- two -- a step -- a polymer -- (-- B --) -- 0.1 - 30 -- a weight -- the section -- from -- becoming -- a vinyl chloride -- a system -- a resin -- a constituent -- manufacture -- a method -- it is .

[0010] Hereafter, this invention is explained in detail. The copolymer which contains a vinyl chloride 80% of the weight or more besides a polyvinyl chloride can be used for the vinyl chloride system resin (A) used by this invention. As a vinyl chloride and a monomer which can be copolymerized, ethylene, a propylene, vinyl bromide, a vinylidene chloride, vinyl acetate, an acrylic ester, a methacrylic ester, etc. are mentioned.

[0011] Next, a two-step polymer (B) is explained. As an acrylic ester used by this invention, the thing of 2-10 has the desirable carbon number of an alkyl group, for example, ethyl-acrylate, acrylic-acid propyl, acrylic-acid n-butyl, isobutyl acrylate, acrylic-acid hexyl, acrylic-acid octyl, and acrylic-acid 2-ethylhexyl or an acrylic-acid benzyl is mentioned. As a methacrylic ester, the thing of carbon numbers 2-4 is desirable, for example, an ethyl methacrylate, a methacrylic-acid propyl, a methacrylic-acid isopropyl, methacrylic-acid n-butyl, a methacrylic-acid isobutyl, methacrylic-acid tertiarybutyl, or a methacrylic-acid benzyl is mentioned.

[0012] Moreover, one or more sorts chosen from an aromatic vinyl compound, a vinylcyanide compound, etc. can be used for the monomer which can be copolymerized, styrene, alpha-substitution styrene, nuclear-substitution styrene and its derivative, for example, an alpha methyl styrene, crawl styrene, vinyltoluene, etc. are mentioned as an aromatic vinyl compound, and acrylonitrile, a methacrylonitrile, etc. are mentioned as a vinylcyanide compound. According to the purpose of using the modifier for vinyl chloride system resins, this monomer can be chosen suitably and can be used.

[0013] In the 1st step of polymerization, it carries out so that other methacrylic esters excluding [ a methyl methacrylate ] an acrylic ester or a methyl methacrylate may become 0 - 40% of the weight 100 to 60% of the weight. If a methyl methacrylate is less than 60 % of the weight, compatibility with a vinyl chloride system resin gets worse, the processability grant effect made into the purpose is not acquired, and the transparency of mold goods gets worse and is not desirable.

[0014] About the 2nd step, the polymerization of the monomer in which a methacrylic ester or an acrylic ester, and copolymerization are possible, or the monomer mixture is carried out to the bottom of the existence of 99 - 70 % of the weight of copolymers obtained in the 1st step 30 to 1% of the weight. If the 1st step of copolymer exceeds 99 % of the weight, a fish eye (non-gelled object) becomes easy to generate and is not desirable in mold goods. Moreover, the 2nd step of heat of polymerization becomes large, a low-molecular-weight portion increases, molecular weight distribution spread, and less than 70% of the weight of a case does not have the difficultly desirable improvement of a plate out.

[0015] The two-step polymer (B) of this invention is obtained by adding and carrying out the emulsion polymerization of the carbonate and sodium hydroxide, or potassium hydroxide of alkali metal to the above-mentioned component an emulsifier and a polymerization initiator, and if needed. what has a well-known emulsifier -- it can be used -- moreover -- as a polymerization initiator -- water solubility -- the thing of oil-soluble and a redox system can be used

[0016] The polymerization method of this invention can be performed like the usual emulsion-polymerization method, heating more than the decomposition temperature of the polymerization initiator to be used. In addition, in this polymerization reaction, since the molecular weight and molecular weight distribution of a copolymer which are obtained have big influence on the property as processing aid, it is desirable to adjust molecular weight etc., and using a chain transfer agent. [ setting up polymerization conditions suitably ]

[0017] In case the 1st step of creation of a copolymer is not dropped over a long time as the regulation method, but a random copolymer is created and the polymerization of the 2nd step is carried out to the bottom of existence of the copolymer, it adds by the method (dropped for a short time) near a package or it. That is, etasp/c of the two-step polymer (B) obtained adjusts so that 0.05 or more and molecular weight distribution may become 3.0 or less. Since a low-molecular-weight portion increases and molecular weight distribution spread when etasp/c is less than 0.05, generating of a plate out is seen and it is not desirable.

[0018] By washing [ separate this and ] and being powdered, collecting the generated copolymer latexes after a polymerization-reaction end, a salting-out or after carrying out \*\*\*\* solidification and making it precipitate, or performing spray drying or freeze drying, it is powdered and collects.

[0019] It is called a 2 step (polymer B) (less or equal and "processing aid". When blending) with a vinyl chloride system resin, it is in a powder state preferably, for example, mixes using a ribbon blender or a Henschel mixer. Moreover, when carrying out a fabricating operation, for example, after kneading using a roll mill or a Banbury mixer, an extruder or a calendering-roll machine performs.

[0020] The loadings of this processing aid are 0.1 - 30 weight section to the vinyl chloride system resin 100 weight section. When loadings are under the 0.1 weight section, improvement of the processability of a resin is inadequate, and when exceeding 30 weight sections, the mechanical property which the resin originally has will be spoiled and it is not desirable.

[0021] In addition, when blending the processing aid of this invention with a vinyl chloride system resin, a well-known stabilizer, a plasticizer, lubricant, a coloring agent, a shock-proof modifier, etc. can also be blended collectively if needed.

[0022]

[Example] Hereafter, although this invention is explained in more detail based on an example, this invention is not limited at all by these. In addition, the "section" in an example and the example of comparison and "%" express the "weight section" and "weight %" respectively.

[0023] The ion-exchange-water 150 section which replaced dissolved oxygen by the example 1 reaction container with nitrogen, and the dialkyl sodium-succinate 1.5 section and the potassium persulfate 0.3 section were taught. Subsequently, agitating, the mixture which consists of the methyl-methacrylate 80 section, the butyl-acrylate 5 section, and the normal octyl mercaptan 0.02 section was taught, the temperature up of the reaction container was carried out to 65 degrees C, it held for 2 hours, and the 1st-step polymerization was performed. The package injection of the mixture which consists of the methyl-methacrylate 5 section and the butyl-acrylate 10 section into a reaction container after that was carried out, it held at this temperature after an injection for 3 hours, the 2nd-step polymerization was performed, and the copolymer latex was obtained. The copolymer added and generated in 2.0% of aluminum-sulfate solution was made to precipitate, agitating the obtained copolymer latex. Subsequently, after isolating the copolymer which precipitated preparatively, each processing of washing, dehydration, and dryness was performed, and powdered processing aid was obtained.

[0024] an example 2 -- processing aid was obtained like the example 1 except having taught the mixture which consists the 1st-step polymerization of the methyl-methacrylate 80 section, the methacrylic-acid butyl 5 section, and the octyl mercaptan 0.02 section

[0025] an example 3 -- processing aid was obtained like the example 1 except having made the 2nd-step polymerization into the methyl-methacrylate 5 section and the ethyl-methacrylate 10 section

[0026] an example 4 -- processing aid was obtained like the example 1 except having supplied the mixture of the methyl-methacrylate 5 section and the butyl-acrylate 10 section in 5 minutes, and having performed the 2nd-step polymerization

[0027] an example 5 -- processing aid was obtained like the example 1 except having supplied the mixture of the methyl-methacrylate 5 section and the butyl-acrylate 10 section in 10 minutes, and having performed the 2nd-step polymerization

[0028] an example 6 -- processing aid was obtained like the example 1 except having supplied the mixture of the methyl-methacrylate 5 section and the butyl-acrylate 10 section in 15 minutes, and having performed the 2nd-step polymerization

[0029] an example 7 -- processing aid was obtained like the example 1 except having carried out by teaching the mixture which consists the 1st-step polymerization of the methyl-methacrylate 66 section, the butyl-acrylate 5 section, and the normal octyl mercaptan 0.02 section, having supplied the mixture of the methyl-methacrylate 20 section and the butyl-acrylate 9 section, and having performed the 2nd-step polymerization

[0030] an example 8 -- processing aid was obtained like the example 1 except having carried out by teaching the mixture which consists the 1st-step polymerization of the methyl-methacrylate 87 section and the butyl-acrylate 5 section, having supplied the mixture of the methyl-methacrylate 4 section and the butyl-acrylate 4 section, and having performed the 2nd-step polymerization

[0031] Processing aid was obtained like the example 1 except having changed the example 9 butyl acrylate into the ethyl acrylate, and having performed the polymerization.

[0032] Processing aid was obtained like the example 1 except having changed the amount of example 10 normal octyl mercaptans into the 0.1 sections, and having performed the polymerization.

[0033] Processing aid was obtained like the example 1 except having changed the amount of example 11 normal octyl mercaptans into the 0.2 sections, and having performed the polymerization.

[0034] The mixture of the methyl-methacrylate 73 section, the ethyl-acrylate 18 section, and the normal octyl mercaptan 0.03 section was taught, the temperature up of the reaction container was carried out to 65 degrees C, it held in the ion-exchange-water 200 section which replaced dissolved oxygen by the example of comparison 1 reaction container with nitrogen, the dialkyl sulfo sodium-succinate 1.5 section, and the ammonium-persulfate 0.2 section for 4 hours, and the 1st-step polymerization was performed in them. After that, it added having applied the methyl-methacrylate 9 section for 30 minutes into the reaction container, the polymerization was terminated in 30 minutes after addition per hour, and the copolymer latex was obtained. The copolymer added and generated in 2.0% of aluminum-sulfate solution was made to precipitate, agitating the obtained copolymer latex. Subsequently, after isolating the copolymer which precipitated preparatively, each processing of washing, dehydration, and dryness was performed, and powdered processing aid was obtained (the example 1 and these conditions in JP,52-1745,B).

[0035] the example 2 of comparison -- processing aid was obtained like the example 1 of comparison except having taught the mixture of the methyl-methacrylate 9 section and the methacrylic-acid butyl 1 section for the 2nd-step polymerization (the example 1 and these conditions in JP,52-1746,B)

[0036] The ion-exchange-water 200 section which replaced dissolved oxygen by the example of comparison 3 reaction container with nitrogen, and the sodium dodecylbenzenesulfonate 2 section and the ammonium-persulfate 0.1 section were taught. Subsequently, the temperature up of the contents was carried out to 60 degrees C, agitating, and the monomer mixture which consists of the methyl-methacrylate 75 section and the methacrylic-acid n-butyl 10 section was added over 4 hours and 15 minutes. Heating churning was carried out for after [ an addition end ] 1 hour, and it added, having applied the mixture of the methyl-methacrylate 5 section and the ethyl-acrylate 10 section for 45 minutes, contents were kept at 60 degrees C for after [ an addition end ] 30 minutes per hour, the polymerization was terminated, and the copolymer latex was obtained. Salting-out solidification of this latex was carried out with salt, it filtered, and rinsing dryness was carried out and processing aid was obtained (the example 1 and these conditions in JP,53-2898,B).

[0037] the example 4 of comparison -- it added at it, having applied monomer mixture for 60 minutes at the time of the 1st-step

polymerization, and processing aid was obtained like the example 1 except having carried out the package injection of the monomer mixture at the time of the 2nd-step polymerization

[0038] the example 5 of comparison -- processing aid was obtained like the example 1 except having added at it, having applied monomer mixture for each 30 minutes at the time of the 1st step and 2nd-step polymerization

[0039] the example 6 of comparison -- at the time of the 1st-step polymerization, the package injection of the monomer mixture was carried out, and processing aid was obtained like the example 1 except having added at it, having applied monomer mixture for 30 minutes at the time of the 2nd-step polymerization

[0040] Processing aid was obtained like the example 1 except having changed the amount of example of comparison 7 normal octyl mercaptans into the 0.3 sections, and having performed the polymerization.

[0041] the example 8 of comparison -- the mixture which consists of the methyl-methacrylate 45 section, the butyl-acrylate 35 section, and the normal octyl mercaptan 0.02 section performed the 1st-step polymerization, and processing aid was obtained like the example 1 of comparison except having made the 2nd-step polymerization into the mixture of the methyl-methacrylate 15 section and the ethyl-acrylate 5 section

[0042] the example 9 of comparison -- the mixture which consists of the methyl-methacrylate 55 section, the butyl-acrylate 10 section, and the normal octyl mercaptan 0.02 section performed the 1st-step polymerization, and processing aid was obtained like the example 1 of comparison except having made the 2nd-step polymerization into the mixture of the methyl-methacrylate 30 section and the butyl-acrylate 5 section

[0043] After blending with each common combination composition of the dibutyl tin mercapto 1.5 section, the butyl-stearate 1 section, and the lubricant 0.7 section the 3 sections of processing aid obtained in the above-mentioned examples 1-11 and the examples 1-7 of comparison, respectively, using the Henschel mixer, in the vinyl chloride system resin 100 section of the adjustment average degree of polymerization 700 of a vinyl chloride system resin constituent, it mixed until it became 120 degrees C, and the vinyl chloride system resin constituent was obtained to it at it.

[0044] Many physical properties were measured by the following examining method using the obtained resin constituent. An evaluation result is shown in Table 1 and 2.

(1) Polymerization invert ratio : the polymerization invert ratio of each monomer was calculated using the gas chromatograph.

(2) Aggregate : the obtained latex was filtered at the wire gauze of 200mesh(es), and the aggregate which has not been filtered was dried and calculated.

(3) In etasp/c: 100ml chloroform, 0.1g of obtained polymer latexes was dissolved, and it measured at 25 degrees C using the Ostwald viscometer.

(4) Molecular weight distribution (Mw/Mn) : 0.2g of obtained polymer latexes was dissolved in the 100ml tetrahydrofuran, and it measured using column GPC-8025, GPC-804, and GPC-805 by the Shimazu high-speed liquid chromatograph.

[0045] (5) Gelling property : the time Tmax (sec) until it results in maximum torque Mmax (kg-m) and Mmax when measuring using a Brabender PURASUCHI coder on the temperature of 160 degrees C, rotational frequency 30rpm, the sample fill of 50g, and the conditions for preheating 5 minutes was shown.

(6) Using the flow mark and plate-out: 6 inch test roll, 100g of samples predetermined on conditions with the temperature of 180 degrees C, roll-before rotational frequency 12rpm, a post-roll 16rpm, and a roll interval of 0.2mm was kneaded for 5 minutes, and about 0.2mm sheet was obtained. The front face of the sheet was observed and it judged by the size of the flow mark and thickness, and thinness. Moreover, the plate out observed the roll front face after kneading, and judged it in the amount of the residue adhering to the roll front face.

(7) Tdie (100mm width of face) was attached in the (fish eye FE): 25phi extruder, and it was set as temperature C1 160 degree C, C2 170 degree C, C3 180 degree C, and Tdie 190 degree C, and by rotational frequency 40rpm, the film (0.1mm) of a predetermined sample was extruded and visual evaluation was carried out from the number of FEs in the fixed area on the front face of a film.

[0046] Criterion; it is very fitness O. Fitness O. Inferior \*\*. Very inferior x.

[0047]

[Table 1]

[0048]

[Table 2]

| 性<br>(kg-m) | フロマー | プレアット | FE |
|-------------|------|-------|----|
| 6.2         | △    | △     | △  |
| 6.1         | △    | △     | △  |
| 6.0         | ×    | △     | ◎  |
| 6.1         | △    | △     | ◎  |
| 6.1         | ×    | ○     | ◎  |
| 6.1         | ×    | ×     | ◎  |
| 6.2         | ○    | ×     | ◎  |
| 6.3         | ×    | ×     | ◎  |
| 6.4         | ×    | ×     | ◎  |

|        | 重合率<br>(%)          | 凝集物<br>(%) | $\eta_{SP}/C$ | 分子重<br>平均 | ゲル化特性<br>T <sub>max</sub> (sec) | M <sub>max</sub> (kg-m) | フロマー | プレアット | FE |
|--------|---------------------|------------|---------------|-----------|---------------------------------|-------------------------|------|-------|----|
|        |                     |            |               |           |                                 |                         |      |       |    |
| 実施例-1  | MMA 99.9<br>BA 99.8 | 0.01以下     | 0.400         | 2.3       | 12                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-2  | MMA 99.9<br>BA 99.8 | 0.01以下     | 0.396         | 2.4       | 14                              | 6.1                     | ◎    | ◎     | ○  |
| 実施例-3  | MMA 99.9<br>BA 99.8 | 0.01以下     | 0.392         | 2.6       | 13                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-4  | MMA 99.9<br>BA 99.8 | 0.01以下     | 0.398         | 2.5       | 12                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-5  | MMA 99.9<br>BA 99.9 | 0.01以下     | 0.394         | 2.7       | 12                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-6  | MMA 99.9<br>BA 99.9 | 0.01以下     | 0.392         | 2.8       | 12                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-7  | MMA 99.9<br>BA 99.6 | 0.01以下     | 0.390         | 2.9       | 10                              | 6.2                     | ○    | ○     | ◎  |
| 実施例-8  | MMA 99.9<br>BA 99.9 | 0.01以下     | 0.403         | 2.1       | 14                              | 6.0                     | ◎    | ◎     | ◎  |
| 実施例-9  | MMA 99.9<br>EA 95.0 | 0.01以下     | 0.401         | 2.2       | 12                              | 6.1                     | ◎    | ◎     | ◎  |
| 実施例-10 | MMA 99.8<br>BA 99.7 | 0.01以下     | 0.202         | 2.3       | 11                              | 6.2                     | ◎    | ○     | ◎  |
| 実施例-11 | MMA 99.8<br>BA 99.6 | 0.01以下     | 0.09          | 2.6       | 9                               | 6.2                     | ◎    | ○     | ◎  |

※MMA：メチルメタクリレート、BA：アクリル酸ブチル、EA：アクリル酸エチル、BMA：メタクリル酸ブチル、EMA：メタクリル酸エチル

|       | 重合率<br>(%)   | 粘度<br>(cP) | SP/C  | GPC<br>分子量分布 | ゲル化性                   |                  |
|-------|--------------|------------|-------|--------------|------------------------|------------------|
|       |              |            |       |              | T <sub>max</sub> (sec) | M <sub>max</sub> |
| 比較例-1 | 99.9<br>99.6 | 0.02       | 0.360 | 3.2          | 8                      |                  |
| 比較例-2 | 99.9<br>99.2 | 0.01       | 0.365 | 3.2          | 9                      |                  |
| 比較例-3 | 99.9<br>99.4 | 0.01       | 0.346 | 4.2          | 16                     |                  |
| 比較例-4 | 99.9<br>99.8 | 0.01以下     | 0.345 | 3.7          | 14                     |                  |
| 比較例-5 | 99.9<br>99.8 | 0.01以下     | 0.384 | 4.0          | 12                     |                  |
| 比較例-6 | 99.9<br>99.8 | 0.01以下     | 0.380 | 4.5          | 10                     |                  |
| 比較例-7 | 99.7<br>99.5 | 0.01以下     | 0.04  | 2.8          | 8                      |                  |
| 比較例-8 | 99.9<br>99.3 | 0.02       | 0.346 | 4.0          | 7                      |                  |
| 比較例-9 | 99.9<br>99.9 | 0.05       | 0.345 | 4.2          | 7                      |                  |

※MMA:メチルメタクリレート、BA:アクリル酸ビニル、EA:アクリル酸エチル

[0049]

[Effect of the Invention] From the above result, the processing aid of this invention can press down the flow mark on the improvement of the plate out generated during the fabricating operation of this resin, and the front face of a sheet, and generating of a fish eye by blending this with a vinyl chloride system resin.

[Translation done.]